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**Quaternary Ammonium Halides - Versatile Reagents
for Precipitation Titrations**

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This paper was prepared for submittal
to
J. Chemical Education

August 1985

Lawrence
Livermore
National
Laboratory

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QUATERNARY AMMONIUM HALIDES - VERSATILE REAGENTS FOR PRECIPITATION TITRATIONS

For the study of potentiometric titrations only very simple equipment is required: a buret, a pH/millivolt meter, a reference electrode, and a home-made plastic-coated graphite indicating electrode (1). Quaternary ammonium halides were found very suitable as titrants for precipitation titrations (2). We recommend cetylpyridinium chloride (CPC), a compound which is relatively non-toxic, inexpensive, and very versatile. It can be used for the determination of many inorganic and organic anions. Many cations can be determined after conversion to their halide or cyanide complexes.

BACKGROUND

Willard and Smith (3) recommended tetraphenylarsonium chloride ($\phi_4\text{AsCl}$) for the gravimetric determination of some large anions and some complex halides. In 1968 Baczuk and DuBois (4) used $\phi_4\text{AsCl}$ for the potentiometric titration of perchlorate, using a perchlorate ion-selective electrode (ISE). We have found that quaternary ammonium halides can replace $\phi_4\text{AsCl}$ as the titrant in this and many other titrations (5). In earlier work we used cetyltrimethylammonium bromide (CETAB) as titrant (6). Recent work has shown that CPC is preferable because of its higher solubility in water, which makes it possible to use more concentrated titrant solutions (2). We have also replaced the fairly expensive commercial ISE's with inexpensive home-made plastic-coated graphite indicating electrodes (1).

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract no. W-7405-ENG-48.

EXPERIMENTAL

The preparation of the polyvinyl(chloride)/dioctylphthalate-coated graphite rod was described previously in this Journal (1). The titrant was a 0.01 M aqueous solution of cetylpyridinium chloride which is available from various suppliers.¹ It was prepared by dissolving 3.58 g of the monohydrate in approximately 250 ml of warm water, and diluting to volume with cold distilled water.

Determinations of 0.025 mmol of analyte were made in a volume of 25 ml. Potentiometric titrations may be performed using an automatic titration apparatus, or by manually adding increments of titrant, letting the emf equilibrate, taking emf reading, etc., and finally drawing a titration curve. If this latter method is used, it is helpful for endpoint calculation to add equal increments of titrant in the endpoint region according to the method of Lingane (7).

The experimental conditions, sample titration curves, and statistics of recoveries have been described in a review of the analytical applications of quaternary ammonium halides (2) and some recent work (8,9). A brief summary of the feasible pH ranges is presented in Tables 1, 2, and 3. This should help in getting the student started without having to refer to the literature.

For the experiments reported in Tables 1 and 2, the titrant was mainly CETAB. As stated previously, this titrant was replaced in later experiments with CPC. A single experiment in Table 2, using CPC, gives an indication of

¹Aldrich catalog no. 85,556-1, Alfa catalog no. 13,651; Eastman catalog no. P5361. The reagent from Alfa was the least expensive material. One liter of a 0.01 M solution costs \$0.17.

the improvement in the magnitude of endpoint breaks possible with this titrant. The student may want to verify this for some of the results reported in Tables 1 and 2.

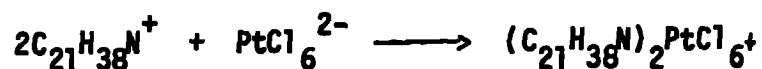
In most of the experiments reported in Tables 1 and 2, a fluoroborate ISE was used. As reported elsewhere(1), a coated-graphite sensor can be used for all the experiments mentioned in this paper. Again, a comparison of the coated-graphite sensor with those used previously is invited. Obviously, this electrode, as well as some of the so-called "ion-selective" electrodes, are quite non-selective.

More recent work using CPC as titrant and the coated-graphite sensor is summarized in Table 3.

A few conditioning runs should precede each experiment. This is also good practice when working with ISE's. In highly acidic solutions the coated graphite indicating electrode will deteriorate more quickly than in other media. This requires re-coating of the graphite sensor as outlined in reference (1).

INORGANIC ANIONS

A list of inorganic anions that can be determined with CPC is given in Table 4. Many anions can be titrated, with the exception of those of the elements of groups 1A through VB and group VIII. Cations in group VIII can easily be converted to their halides by adding an excess of potassium bromide or chloride in acid solutions. A large number of complex cyanides can similarly be determined, some in acid solutions because of their great



stability. A typical reaction, for the determination of Pt^{4+} , is given by the equation. In many cases the bromide complex will yield sharper titration curves than the corresponding chloride because of the lower solubility of the resulting cetylpyridinium precipitate.

Table 4 is not complete and many other applications are no doubt possible. Determinations of the stoichiometry of some of these reactions yielded rather unexpected results. For instance, the titration of Bi^{3+} in acid solution in the presence of excess bromide required 1.5 mole of CPC per Bi^{3+} . The composition of the resulting precipitate conformed, according to elemental analysis, to the formula $(\text{C}_{21}\text{H}_{38}\text{N})_3\text{Bi}_2\text{Br}_7$, calculated percent. C 40.02, H 6.08, N 2.22; found percent. C 39.55, H 6.03, N 2.21 (9). Molybdates and tungstates form isopoly and heteropoly compounds which are quite sensitive to pH and yield complex compounds in the titration.(10)

ORGANIC ANIONS

A list of some organic anions that were titratable vs quaternary ammonium halides is presented in Table 2. While in earlier work CETAB was used, recent work shows that CPC is preferable. Only water-soluble compounds can be determined because nonaqueous, or partially nonaqueous media will dissolve the organic coating of the graphite indicating electrode. However, many alkali metal salts of organic acids and dyes are water soluble and thus can be determined. It should be noted that a minimum of 10 carbon atoms is required in the analyte for the successful titration of soaps and anionic detergents.

CONCLUDING REMARKS

We have shown numerous applications of quaternary ammonium halides for the determination of inorganic and organic anions. It is left up to the ingenuity of the student to investigate additional anions and to devise possible separations. Thus based on previously published data, the following separations are feasible:

1. Ti^{3+} as the halide in the presence of Ti^{+} .
2. Te^{4+} as the halide in the presence of Te^{6+} .
3. Te^{4+} as the halide in the presence of Se.
4. Ga^{3+} as the halide in the presence of In^{3+} .

These relatively non-toxic, inexpensive titrants can be used for more precipitation titrations of anions than any previously used titrant.

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Table 1. Optimum and feasible pH ranges for the determination of inorganic anions with CETAB, using the fluoroborate ISE (2)

Anion	Mean endpoint break, mV	Optimum ⁺ pH range	Feasible ⁺ pH range
ClO ₄	65	4.0 - 8.0	1.2 - 12.8
BF ₄	50	4.0 - 8.0	2.3 - 10.6
MnO ₄	125	2.9 - 7.0	1.8 - 10.7
ReO ₄	45	4.0 - 8.0	1.9 - 11.0
PF ₆	150	2.1 - 7.9	1.5 - 10.6
AsF ₆	175	4.0 - 8.0	1.8 - 10.6
AuCl ₄	250	1.5 - 2.7	≤2.75
TlCl ₄	200	2.3	0.2 - 4.0
*I ⁻	35	2.7 - 10.7	1.8 - 10.7
*IO ₄	30	4.0 - 6.0	1.6 - 7.3
PdCl ₄	15	2.2 - 5.7	≤5.7
*SbF ₆	85	3.0 - 5.0	1.8 - 7.7
Cr ₂ O ₇	70	0.65	0 - 11.3
Fe(CN) ₆	95	1.9 - 9.6	1.0 - 11.3
HgCl ₄	60	0.65 - 2.3	0 - 9.4
PtCl ₄	35	0.65	0 - 2.0
SnCl ₄	50	6 N HCl	
SnCl ₆	45	1 N HCl	
S ₂ O ₈	70	7 - 10	2.5 - 11.3
PtCl ₆	100	2.2 - 9.75	0.35 - 12.1
OsCl ₆	125	1.9 - 8.4	0.2 - 8.4
Fe(CN) ₆	65	1.8 - 2.2	1.8 - 10.0
IrCl ₆	40	2.7 - 7.8	1.7 - 8.0

*Not analytically useful, because endpoint breaks are very gradual.

+Within the optimum pH ranges the steepest endpoint breaks are obtained; "feasible" pH ranges include the regions where the breaks are less steep.

Table 2. Some analytical data for the determination of organic anions with quaternary ammonium halides(2)

Anion	Electrode	Titrant	Mean endpoint break, mV	Optimum pH range	Feasible pH range
Nitroform	BF ₄	CETAB	150	7.0 - 10.0	1.5 - 12.2
Nitroform	BF ₄	CPC	165	7.0 - 10.0	1.5 - 12.2
Nitroform	divalent	CETAB	140	7.0 - 10.0	1.5 - 12.2
Nitroform	Ca ²⁺	CETAB	130	7.0 - 10.0	1.5 - 12.2
2,4,5-trichlorobenzenesulfonate	BF ₄	CETAB	110	4.0 - 12.0	0.2 - 12.3
2,4-dinitrobenzenesulfonate	BF ₄	CETAB	50	≥2	1.4 - 11.3
Picrylsulfonate	BF ₄	CETAB	110	6.0 - 10.0	1.7 - 12.2
Tetraphenylborate	BF ₄	CETAB	450	≥8	1.6 - 12.0
Cyanotriphenylborate	BF ₄	CETAB	330	8.0 - 12.0	1.8 - 12.0
Picrate	BF ₄	CETAB	180	5.0 - 7.0	2.1 - 9.2
Dodecyl sulfate	BF ₄	CETAB	220	5.5 - 9.8	2.1 - 12.2
Bromophenol blue	BF ₄	CETAB	175	1.0 - 2.0	0.8 - 3.1
Bromocresol purple	BF ₄	CETAB	200	1.8 - 2.2	1.0 - 2.5
Bathophenathroline disulfonic acid disodium salt, trihydrate	BF ₄	CETAB	45	8.6 - 10.4	6.2 - 12.0

Table 3. Conditions for the potentiometric titration of some anions with CPC, using a coated-graphite sensor (8,9)

Ion determined	Optimum pH/ acidity	Feasible pH/ acidity	Remarks
AuCl₄	0.5 - 1	<0 - 5	at pH >2 curve has 2 inflections
PtCl₄	1.15		in aqueous solution rapid oxidation occurs
PtCl₆	0.5 - 1	<0 - 2	at pH >2 curve has 2 inflections
PdCl₄	1 - 2	0.65 - 4.1	
PdCl₆	0.5 - 1	0.15 - 4.1	ppt. formed is reduced to the PdCl₄ salt
OsCl₆	0.5 - 1	0 - 6.3	
IrCl₆	5.5 - 8	1.8 - 10	not analytically useful: shallow breaks
IrCl₆	3 - 7	0.8 - 7	
Ru₂Cl₁₀	1.7 - 2.4		not analytically useful: shallow breaks
RhCl₆	1.8 - 2.1		not analytically useful: rapid decomposition
ReO₄	2.0 - 9.0	1.1 - 11.5	
SbCl₅	3 M HCl	1 - 6 M HCl	
Bi₂Br₇	0.2 - 0.5 M HNO₃	0.1 - 1 M HNO₃	70 - 200-fold excess KBr required
GaCl₄	conc. HCl	6 - 12 N HCl	in presence of excess LiCl the acidity may be reduced

Table 4. Some Inorganic Anions Titratable vs CPC, Classified According to Subgroups of the Periodic Table.

VIB	VIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	
$\text{Cr}_2\text{O}_7^{2-}$	MnO_4^-	<u>cyanides</u>	<u>halides</u>	AuCl_4^-	$\text{Zn}(\text{CN})_4^{2-}$	BF_4^-	SnCl_2^{2-}	PF_6^-	$\text{S}_2\text{O}_8^{2-}$	ClO_4^-
MoO_4^{2-}	ReO_4^-	$\text{Fe}(\text{CN})_6^{3-}$	$\text{Ru}_2\text{Cl}_{10}^{4-}$	$\text{Au}(\text{CN})_2^-$	$\text{Hg}(\text{CN})_4^{2-}$	GaCl_4^-	SnCl_4^{2-}	AsF_6^-	TeCl_6^{2-}	IO_4^-
WO_4^{2-}		$\text{Fe}(\text{CN})_6^{4-}$	RhCl_6^{3-}		HgCl_4^{2-}	TlCl_4^-		SbF_6^-		I^-
		$\text{Co}(\text{CN})_6^{3-}$	PdCl_4^{2-}		HgBr_4^{2-}	TlBr_4^-		$\text{Bi}_2\text{Br}_7^{3-}$		
		$\text{Ni}(\text{CN})_4^{2-}$	PdCl_6^{2-}							
		$\text{Pd}(\text{CN})_4^{2-}$	OsCl_6^{2-}							
		$\text{Os}(\text{CN})_6^{4-}$	IrCl_6^{2-}							
		$\text{Pt}(\text{CN})_4^{2-}$	IrCl_6^{3-}							
		$\text{Pt}(\text{CN})_6^{2-}$	PtCl_4^{2-}							
			PtCl_6^{2-}							